## This Page Is Inserted by IFW Operations and is not a part of the Official Record

### **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

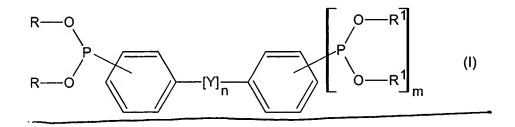
## IMAGES ARE BEST AVAILABLE COPY.

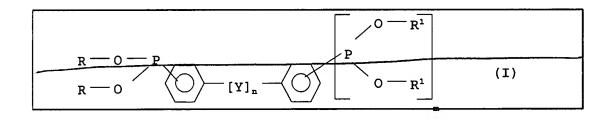
As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

Weber et al., Serial No. 10/018,341

#### **CLAIMS**

- 1. (currently amended) A thermoplastic molding composition comprising
  - A) from 1 to 97.85% by weight of at least one thermoplastic polyester,
  - B) from 1 to 97.85% by weight of at least one polycarbonate,
  - C) from 1 to 50% by weight of an elastomeric polymer,
  - D) from 0.1 to 5% by weight of a phosphorus-containing stabilizer, wherein component D) is composed of an organic phosphonite of the formula (I):





where

- m is 0 or 1,
- n is 0 or 1,
- Y is an oxygen bridge, a sulfur bridge or a 1,4-phenylene bridge, or a bridging unit of the formula –CH(R²)–; each of the R–O– and R¹–O–groups, independently of one another, is the radical of an

Weber et al., Serial No. 10/018,341

aliphatic, alicyclic or aromatic alcohol which may contain up to three hydroxyl groups, but excluding any arrangement of the hydroxyl groups which permits these to be part of a phosphorus-containing ring (termed monovalent R–O–groups), or two R–O– or, respectively, R¹–O- groups, bonded to a phosphorus atom, in each case independently of one another, together are the radical of an aliphatic, alicyclic or aromatic alcohol having a total of up to three hydroxyl groups (termed bivalent R–O–, or, respectively, R¹–O–groups),

- $R^2$  is hydrogen,  $C_1$ – $C_8$ –alkyl or a group of the formula COOR<sup>3</sup>, and  $R^3$  is  $C_{1-8}$ –alkyl or is composed of at least one inorganic salt of phosphoric acids,
- E) from 0.05 to 2 % by weight of an organic acid, and
- F) from 0 to 60% by weight of <u>other additives</u> other conventional additives, where the percentages by weight of components A) to F) give 100%.
- 2. (original) A thermoplastic molding composition as claimed in claim 1, wherein component A) is composed of a polyalkylene terephthalate having from 2 to 10 carbon atoms in the alcohol moiety.
- 3. (previously presented) A thermoplastic molding composition as claimed in claim 1, wherein component E) is composed of citric acid or of p-toluenesulfonic acid or

Weber et al., Serial No. 10/018,341 of mixtures of these.

4-5. (canceled)

6. (previously presented) A molding of any type, obtainable from the thermoplastic molding compositions as claimed in claim 1.

# Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 20: Photography to Plastics, Processing

Editors: Barbara Elvers, Stephen Hawkins, Gail Schulz

Japan

cles

UK

of Germany

ederal Republic of Germany

al Republic of Germany



Numerical data, descriptions of methods or equipment, and other information presented in this book have been carefully checked for accuracy. Nevertheless, authors and publishers do not assume any liability for misprints, faulty statements, or other kinds of errors. Persons intending to handle chemicals or to work according to information derived from this book are advised to consult the original sources as well as relevant regulations in order to avoid possible hazards.

Production Director: Maximilian Montkowski Production Manager: Myriam Nothacker

Editorial Assistants: Ilse Bedrich, Helen Goltz, Reinhilde Gutsche, Monika Pikart-Müller, Philomena

Ryan-Bugler

Library of Congress Card No. 84-25-829

Deutsche Bibliothek, Cataloguing-in-Publication Data:

Ullmann's encyclopedia of industrial chemistry / ed.: Barbara Elvers ... [Ed. advisory board Hans-Jürgen Arpe ...]. — Weinheim; Basel (Switzerland); Cambridge; New York, NY: VCH.

Teilw. executive ed.: Wolfgang Gerhartz

Bis 4. Aufl. u. d. T.: Ullmanns Encyklopädie der technischen Chemie

NE: Gerhartz, Wolfgang [Hrsg.]; Elvers, Barbara [Hrsg.]; Encyclopedia of industrial chemistry

Vol. A. Alphabetically arranged articles.

20. Photography to plastics, processing. - 5. completely rev. ed. - 1992

ISBN 3-527-20120-3 (Weinheim ...) ISBN 0-89573-170-3 (New York)

#### British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

© VCH Verlagsgesellschaft mbH, D-6940 Weinheim (Federal Republic of Germany), 1992. Printed on acid-free paper

Distribution

VCH Verlagsgesellschaft, P.O. Box 101161. D-6940 Weinheim (Federal Republic of Germany)

Switzerland: VCH Verlags-AG, P.O. Box, CH-4020 Basel (Switzerland)

Great Britain and Ireland: VCH Publishers (UK) Ltd., 8 Wellington Court, Wellington Street, Cambridge CB1 1HZ (Great Britain)

USA and Canada: VCH Publishers, 220 East 23rd Street, New York NY 10010-4606 (USA)

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form — by photoprint, microfilm, or any other means — transmitted or translated into a machine language without written permission from the publishers.

Authorization to photocopy items for internal or personal use, or the internal or personal use of specific clients, is granted for libraries and other users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service, provided that the base fee of \$5.00 per copy, plus \$0.50 per page is paid directly to CCC, 27 Congress Street, Salem, MA 01970. 0740-9451/85 \$5.00 + 0.50. Registered names, trademarks, etc. used in this book and not specifically marked as such are not to be considered unprotected.

Cover design: Wolfgang Schmidt

Composition, printing, and bookbinding: Graphischer Betrieb Konrad Triltsch, D-8700 Würzburg

Printed in the Federal Republic of Germany

Vol. A 20

#### **Contents**

Photography .......
Photovoltaic Cells ...
Phthalic Acid and De
Phthalocyanines ....
Pigments, Inorganic ...
Pigments, Organic ...
Plant Growth Regula

#### **Cross References**

Photoresists → Imagin Phototubes → Photoe Phthalic Anhydride → Derivatives Physical Properties, E → 6. Estimation of Pickling → Metals, Su Piezoelectric Materials Pimelic Acid → Dicar Pinacolone → Ketone: Pinch Technology → 1 Pine Oil → Turpentine Piperazine → Amines, Piperidine → Amines,

#### **4.2.** Additives [5], [70] (→ Plastics, Additives)

#### 4.2.1. Overview

592

Polymers are rarely used directly as materials. They do not fulfill per se all technological requirements and become commercially useful only after they have been mixed with certain additives. These additives average ca. 23% of the total weight of plastics (Table 15) but may range for individual plastics from 0% (packaging films for food) to 90% (barium ferrite-filled ethylenevinyl acetate copolymers for magnetizable sealing strips). Their economic value approximates that of plastics because some additives command prices that are a hundred times those of the plastics themselves.

Polymer additives are to be distinguished from polymer auxiliaries; the former are added to polymers after the polymerization process, whereas the latter are used for the manufacture of polymers (e.g., polymerization catalysts, emulsifiers, initiators). The free-radical initiators used for the hardening of unsaturated polyesters

Table 15. Annual U.S. consumption of polymer additives for plastics, 1980 (plastics production: 16076000 t/a)

Additive	Consumption in t/a	
Process additives		
Processing stabilizers		
Heat stabilizers (PVC)	43 000	
Antioxidants	18 000	
Processing aids		
Lubricants, slip agents, etc.	50 000	
Polymeric processing aids	< 1000	
Mold-release agents	< 1000	
Nucleating agents	< 1000	
Radical initiators for thermosets	15000	
Functional additives		
Stabilizing additives		
Antioxidants	see above	
Metal deactivators	< 1000	
Light stabilizers	2 400	
Flame retardants	220 000	
Biostabilizers	< 1000	
Modifiers		
Colorants	150000	
Fillers and reinforcing agents		
Mineral-based	1730 000	
Glass	462 000	
Natural organic	133000	
Synthetic organic	2000	
Plasticizers	1 000 000	
Blowing agents (without gases)	7000	
Impact modifiers	< 5000	
Antistatic agents	2000	
Total	3844400	

are sometimes considered additives (added to the solution of unsaturated polyester molecules in monomers such as styrene) and sometimes auxiliaries (promoting the thermosetting reaction).

Additives are usually subdivided according to their application into process additives and functional additives. Process additives aid the processing of plastics by either stabilizing the chemical composition of polymers (processing stabilizers) or facilitating the processing itself (processing aids). Functional additives stabilize the chemical composition against attacks by environmental agents (stabilizing additives) or improve certain end-use properties (modifiers). Additives may also be classified according to their primary mode of action (chemical or physical). Some additives act in more than one way: a filler or colorant may also be a nucleating agent for crystallization, a pigment may enhance discoloration, etc.

#### 4.2.2. Chemofunctional Additives

Polymers can be attacked by oxygen and ozone during processing and use. The attack generates radicals that cause chain reactions to produce even more radicals. Ultimately, changed chemical compositions, degradation, or crosslinking result. Oxidation is reduced if the accessibility of the oxidizable groups is limited or if radical formation is prevented. Oxygen diffusion into the polymer is slowed by certain coatings that act as mechanical barriers or by additives that diffuse into surface layers and are preferentially oxidized there.

Antioxidants (→Antioxidants) prevent radical formation, at least during processing and for the targeted lifetime of the plastic. They are subdivided into deinitiators and chain terminators.

Deinitiators prevent the formation of radicals (therefore: preventive antioxidants) and are always used in combination with chain terminators (therefore also called secondary antioxidants). They are further subdivided into peroxide deactivators, metal deactivators, and UV absorbers. Peroxide deactivators (tertiary amines, tertiary phosphines, sulfides) convert hydroperoxides into harmless compounds before they can form radicals. Metal deactivators are chelating agents that form inactive complexes with catalytically active metal species (mainly from Ziegler-Natta polymerizations).

Chain terminators, such as hindered phenols, amines, and anellated hydrocarbons, react with

already formed radic ic chain (chain-brea dants). A combination terminators often leatagonistic effects are bon black as filler).

Light-induced de prevented by the redu by the addition of ULess light is absorbe faces are reflective of added (e.g., carbon bi either convert the in infrared radiation or chemical compounds cited states and them

Heat stabilizers t mations of plastics at main application is poly(vinyl chloride) during processing.

Flame retardants cess to burning plast burning gases or by " ated by the burning extinguishing because ates) or water vapor layer are formed (vi treated cellulose) duri bromine compounds burning; these radica from the degradation kinetic chain. Phosph dized during the burn phor oxides, which eit. or are converted by wa that catalyze the elimi

The flammability of terized by the limiting LOI value indicates th ume fraction of oxyge mixture that just allow ter ignition with a LOI > 0.225 are calle with LOI > 0.27, self values (high flammabili oxymethylenes (0.14), saturated polyesters (0 High LOI values are ex ride) (0.32), polybenzin trafluoroethylene (0.95) not absolute measure: combustibility of plast ties also depend on flai

dered additives (added to the ated polyester molecules in tyrene) and sometimes auxilne thermosetting reaction). sually subdivided according 1 into process additives and s. Process additives aid the ics by either stabilizing the on of polymers (processing itating the processing itself unctional additives stabilize sition against attacks by en-(stabilizing additives) or imse properties (modifiers). Adclassified according to their ction (chemical or physical). in more than one way: a filler so be a nucleating agent for igment may enhance discol-

#### ional Additives

De attacked by oxygen and ressing and use. The attack that cause chain reactions to radicals. Ultimately, changed ions, degradation, or crossation is reduced if the accessicable groups is limited or if prevented. Oxygen diffusion solowed by certain coatings ical barriers or by additives rface layers and are preferen-

+Antioxidants) prevent radiast during processing and for e of the plastic. They are subators and chain terminators. event the formation of radiventive antioxidants) and are ibination with chain terminao called secondary antioxifurther subdivided into pers, metal deactivators, and roxide deactivators (tertiary hosphines, sulfides) convert o harmless compounds before icals. Metal deactivators are nat form inactive complexes active metal species (mainly a polymerizations).

rs, such as hindered phenols, ted hydrocarbons, react with

already formed radicals and terminate the kinetic chain (chain-breaking or primary antioxidants). A combination of deinitiators and chain terminators often leads to synergistic effects. Antagonistic effects are also known (e.g., with carbon black as filler).

Light-induced degradation reactions can be prevented by the reduction of light absorption or by the addition of *UV absorbers* and quenchers. Less light is absorbed by the plastic if the surfaces are reflective or if certain pigments are added (e.g., carbon black). Ultraviolet absorbers either convert the incident light into harmless infrared radiation or are transformed into other chemical compounds. Quenchers deactivate excited states and themselves become excited.

Heat stabilizers prevent chemical transformations of plastics at higher temperature; their main application is for the stabilization of poly(vinyl chloride) against HCl elimination during processing.

Flame retardants either prevent oxygen access to burning plastics by formation of nonburning gases or by "poisoning" radicals generated by the burning. Some plastics are selfextinguishing because either CO2 (polycarbonates) or water vapor and a protecting carbon layer are formed (vulcanized fiber: a ZnCl<sub>2</sub>treated cellulose) during burning. Chlorine and bromine compounds generate radicals during burning; these radicals combine with radicals from the degradation of plastics and stop the kinetic chain. Phosphorus compounds are oxidized during the burning to nonvolatile phosphor oxides, which either form a protective layer or are converted by water into phosphorus acids that catalyze the elimination of water.

The flammability of plastics is often characterized by the limiting oxygen index (LOI). The LOI value indicates the limiting value of the volume fraction of oxygen in an oxygen-nitrogen mixture that just allows the polymer to burn after ignition with a flame. Materials with LOI > 0.225 are called flame retardant; those with LOI > 0.27, self-extinguishing. Low LOI values (high flammabilities) are exhibited by polyoxymethylenes (0.14), polyolefins (0.17-0.18), saturated polyesters (0.20), and cellulose (0.20). High LOI values are exhibited by poly(vinyl chloride) (0.32), polybenzimidazole (0.48), and polytetrafluoroethylene (0.95). However, LOI values are not absolute measures of the flammability or combustibility of plastics because these properties also depend on flame temperatures, heat capacities, heat conductivities, melting temperatures, and melt viscosities. The hazard of burning plastics is also determined by smoke formation and the toxicity of the evolving gases.

#### 4.2.3. Processing Aids

Processing aids facilitate the processing of plastics by enhancing either transport rates to the processing machines, flow behavior in these machines, achievement of final properties during processing, or removal of shaped articles from the machines or from each other.

Easy-flow grades of powdered polystyrenes, for example, often contain 3-4% mineral oil, which forms a low-viscosity film on the surface of the particles and thus reduces friction in polar polymers; amphiphilic compounds such as metal stearates or fatty acid amides are used for this purpose. Such external lubricants also reduce the friction between polymer particles and the walls of the processing machine and the friction of polymer melts at such walls; they also prevent the cleavage of particles to smaller flow units. External lubricants are always incompatible with polymers and are thus found predominantly at polymer surfaces. They are related to release agents, which facilitate the separation of shaped articles from the tools (molds), and slip agents, which prevent the sticking together of shaped articles. Slip agents are thus sometimes also called lubricants.

Internal lubricants improve the flow behavior and homogeneity of polymer melts; they also reduce the Barus effect (see Section 7.3.2) and the melt fracture. Internal lubricants probably act by desegregating larger units (aggregates), which were probably formed during polymerization and are still present shortly after the melting of the polymer to a macroscopically homogeneous material. Typical internal lubricants are amphipolar compounds, e.g., modified esters of long-chain fatty acids.

Nucleating agents promote the crystallization of crystallizable polymers by generating many nuclei for crystallites. They prevent the formation of larger spherulites and thus improve the mechanical properties of plastics.

#### 4.2.4. Extending and Reinforcing Fillers

Fillers are solid inorganic or organic materials. Some fillers are added mainly to improve the

economics of expensive polymers; they are extenders. Extenders are usually particulate materials of corpuscular nature, such as chalk and glass spheres (aspect ratio ca. 1). Other fillers are reinforcing agents ("active fillers"); they improve certain mechanical properties. Reinforcing agents possess aspect ratios higher than 1; they may be short fibers, platelets (e.g., kaolin, talc, mica) (→ Reinforced Plastics), or long fibers (continuous filaments). Active fillers are sometimes subdivided into property enhancers (aspect ratio < 100) and true reinforcing fillers (aspect ratio > 100). No sharp dividing line exists between fillers and reinforcing agents, nor can the term "reinforcement" be unambiguously defined (e.g., it may denote an increase in breaking or impact strength or a decrease of brittleness).

A variety of fillers are used for plastics (Table 16).

Glass-fiber-reinforced polymers often carry the abbreviation GRP (or FRP); those reinforced by synthetic organic fibers, CRP. Syntactic plastics are polymers reinforced with hollow glass spheres. The amounts of fillers added vary widely: in general, industry standards are about 30 wt% for thermoplastics and 60 wt% for thermosets.

Fillers act very differently in polymers. Some fillers form chemical bonds with polymers; an example is carbon black, which acts as a chemical cross-linker in elastomers. Other fillers can adsorb polymers on their surfaces: that is, physical bonds are introduced between fillers and polymers. On impact, adsorbed chain segments may take up energy and slip from the surface, which increases impact strength. Still other fillers act as nucleating agents in crystallizable polymers. Fillers furthermore constitute impenetrable walls to polymer coils. They restrict the number of conformational positions of chain segments near the filler surface; chains become less flexible, and tensile strengths and moduli of elasticity increase.

Table 16. Fillers for thermoplastics (T), thermosets (D), and elastomers (E). For definition of other acronyms see Table 1

Filler	Application in	Concentration in %	Improved property
Inorganic fillers			
Chalk	PE, PVC, PPS, PB, UP	< 33 in PVC	price, gloss
Potassium titanate	PA	40	dimensional stability
Heavy spar	PVC, PUR	< 25	density
Talc	PUR, UP, PVC, EP, PE, PS, PP		white pigment, impact strength, plasticizer up- take
Minn	PUR, UP	< 25	dimensional stability,
Mica	rok, or		stiffness, hardness
W = -1!	UP, vinyls	< 60	demolding
Kaolin	T, D	< 40	modulus of elasticity,
Glass spheres	Ι, D		shrinkage, compressive strength, surface prop- erties
Glass fibers	T, D	< 40	fracture strength, impact strength
Fumed silica	T, D :	< 3	tear strength, viscosity (increase)
Quartz	PE, PMMA, EP	· < 45	heat stability, fracture
Sand	EP. UP. PF	< 60	shrinkage (decrease)
Al, Zn, Cu, Ni, etc.	PA, POM, PP	< 100	conductivity (heat and electricity)
MaO	UP	< 70	stiffness, hardness
MgO ZnO	PP, PUR, UP, EP	< 70	UV stability, heat con- ductivity
Organic fillers			
Carbon black	PVC, HDPE, PUR, PI, PE, E	< 60	UV stability, pigmenta- tion, cross-linking
Graphite	EP, MF, PB, PI, PPS, UP, PMMA, PTFE	< 50	stiffness, creep
Wood flour	PF, MF, UF, UP	< 5	shrinkage (decrease), im- pact strength
Starch	PVAL, PE	· < 7	biological degradation

#### 4.2.5. Plasticizers (→ Pl

Plasticizers are added 1 their flexibility, processi About 500 different types keted. They are generall; uids; polymer plasticize smaller amounts. Of all moplastics, 80-85% are chloride); the most impo (2-ethylhexyl)phthalate DOP). The main plastic mineral oil; tires contain plasticizers are mainly al polyethers. The former ar densation; they thus poss mass distributions and al and oligomeric molecule average molar mass is lov are called oligomer plas can also be achieved by c parent monomer with ce: this effect is called inte analogy to external plasti and low molar mass plas

External plasticizers a mary and secondary one interact directly with chai Secondary plasticizers are can be used only in comb plasticizer. A certain pla primary or a secondary chemical constitution of oils are, for example, p polydienes but extender ride).

#### 4.2.6. Colorants

Colorants are subdiv in polymer matrix) and pi tile fibers are dyed mainly preferred for plastics beci lightfastness and are moi tion than dyes. Colorant nated by titanium dioxide black (20%); only 2% a

Pigment particles gene of 0.3-0.8 µm, which allo films and fibers of > 20films and fibers are colorate pigments because these smaller diameters than in

fibers, CRP. Syntactic plasinforced with hollow glass of fillers added vary widely: tandards are about 30 wt% id 60 wt % for thermosets. fferently in polymers. Some I bonds with polymers; an ack, which acts as a chemilastomers. Other fillers can their surfaces: that is, physoduced between fillers and t, adsorbed chain segments and slip from the surface, ict strength. Still other fillers ents in crystallizable polymore constitute impenetracoils. They restrict the numional positions of chain iller surface; chains become sile strengths and moduli of

ion of other acronyms see Table 1

% Improved property

price, gloss dimensional stability density white pigment, impact strength, plasticizer uptake dimensional stability, stiffness, hardness demolding modulus of elasticity, shrinkage, compressive strength, surface properties fracture strength, impact strength tear strength, viscosity (increase) heat stability, fracture shrinkage (decrease) conductivity (heat and electricity) stiffness, hardness UV stability, heat conductivity

UV stability, pigmentation, cross-linking stiffness, creep shrinkage (decrease), impact strength biological degradation

#### 4.2.5. Plasticizers (→ Plasticizers)

Plasticizers are added to polymers to improve their flexibility, processibility, or foamability. About 500 different types of plasticizers are marketed. They are generally low molar mass liquids; polymer plasticizers are used in much smaller amounts. Of all plasticizers for thermoplastics, 80-85% are used for poly(vinyl chloride); the most important plasticizer is di-(2-ethylhexyl)phthalate ("dioctyl phthalate," DOP). The main plasticizer for elastomers is mineral oil; tires contain up to 40%. Polymer plasticizers are mainly aliphatic polyesters and polyethers. The former are prepared by polycondensation; they thus possess fairly broad molar mass distributions and also contain monomeric and oligomeric molecules. Since their numberaverage molar mass is low (ca. 4000 g/mol), they are called oligomer plasticizers. Plasticization can also be achieved by copolymerization of the parent monomer with certain other monomers; this effect is called internal plasticization, in analogy to external plasticization by added high and low molar mass plasticizers.

External plasticizers are subdivided into primary and secondary ones. Primary plasticizers interact directly with chains by way of solvation. Secondary plasticizers are merely extenders; they can be used only in combination with a primary plasticizer. A certain plasticizer may thus be a primary or a secondary one, depending on the chemical constitution of the polymer. Mineral oils are, for example, primary plasticizers for polydienes but extenders for poly(vinyl chloride).

#### 4.2.6. Colorants

Colorants are subdivided into dyes (soluble in polymer matrix) and pigments (insoluble). Textile fibers are dyed mainly with dyes. Pigments are preferred for plastics because they have a higher lightfastness and are more stable against migration than dyes. Colorants for plastics are dominated by titanium dioxide (60-65%) and carbon black (20%); only 2% are dyes.

Pigment particles generally possess diameters of  $0.3-0.8~\mu m$ , which allows the pigmentation of films and fibers of  $> 20-\mu m$  thickness. Very thin films and fibers are colored exclusively by organic pigments because these can be ground to much smaller diameters than inorganic ones. The hid-

ing power of pigments increases with increasing difference between refractive indices of pigment and polymer.

Pigments need not have a special affinity for polymers. They must be wettable by the polymer melt, however, which can be achieved by treating them with surfactants. The aggregation of pigments is mainly the result of air inclusions; it can be removed by the application of vacuum. Pigments can be metered into plastics via master batches (in plastics), color concentrates (in plasticizers), or electric charging of the surface of polymer particles in granulate mixers. Up to 1 wt% of pigment can be mixed in by the last method.

#### 4.2.7. Blowing Agents

Foamed plastics (plastic foams, cellular plastics, expanded plastics) are blends of polymers with gases ( $\rightarrow$  Foamed Plastics). They may be rigid (glass transition or melting temperature higher than use temperature) or flexible; their cell structure can be open or closed. The gases may be air, nitrogen, carbon dioxide, fluorinated hydrocarbons, etc.

Plastic foams can be produced by mechanical means (whipping, stirring), physical methods (shock volatilization of liquids, washing-out of solids), or chemical foaming either by internal foaming during the polymerization or by external foaming with chemical blowing agents. Chemical blowing agents are chemical compounds that decompose at elevated temperature with release of gases. The most widely used agent for natural rubber is N, N'-azobisis obutyronitrile  $(CH_3)_2C(CN)-N=N-C(CN)(CH_3)_2$  (AIBN); for plasticized PVC, N,N'-dinitroso dimethyl terephthalamide  $CH_3-N(NO)-CO-(p-C_6H_4)-$ CO-N(NO)-CH<sub>3</sub> (NTA); and for other plastics, 1,1'-azobisformamide  $H_2N-CO-N=N-$ CO-NH<sub>2</sub> (ABFA). Blowing agents are used in amounts of ca. 0.1% to eliminate sinks in injection molding; 0.2-0.8% for injection-molded structural foams; 0.3% for extended profiles; 1-15% for vinyl plastisol foaming; and 5-15% for compression-molded foam products.

#### 4.3. Processing

Many different types of processes exist to convert monomers, prepolymers, or polymers

# Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 21:

Plastics, Properties and Testing to Polyvinyl Compounds

Editors: Barbara Elvers, Stephen Hawkins, Gail Schulz

1992

g, Japan

icles

• •

i, UK

USA

; of Germany

Federal Republic of Germany

:h :ral Republic of Germany



The glass transition temperature of BPA-PC can be increased even further by partial or total replacement of bisphenol A by 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane [8]; glass transition temperatures of ca. 150 to 240 °C can be achieved in this way. These polycarbonates are transparent, tough, and colorless, even at high glass transition temperatures [8]. Their melt viscosities are favorable compared with those of aromatic polyester carbonates, polysulfones, polyethersulfones, and polyetherimides having the same glass transition temperature.

BPA-PC is used in polymer blends (→ Polymer Blends, pp. 292-294). The most important blends are those with acrylonitrile-butadienestyrene (ABS) graft polymers [6], [19], [20] and those with poly(butylene terephthalate) or poly-(ethylene terephthalate), and impact resistance modifiers (e.g., ABS) [6], [19], [21]. Compared to ABS, BPA-PC-ABS blends have improved heat resistance. They also exhibit good processibility, light stability, surface quality, and high toughness, even at low temperature (tough fracture in the notched impact strength test). Blends of BPA-PC with poly(alkylene terephthalates) and impact strength modifiers have a high heat distortion resistance, and high toughness even at low temperature. Their resistance to gasoline and other solvents is better than that of BPA-PC.

### 2.3. Bisphenol A Polycarbonate with Additives

Most of the additives discussed in this section are described in detail elsewhere ( $\rightarrow$ Plastics, Additives).

Mold-Release Agents. The addition of small amounts (< 1 wt%) of mold-release agents (e.g., fatty acid esters of higher alcohols, such as pentaerythritol or glycerol) to the polycarbonate improves the mold release of complicated parts [6]. See also  $\rightarrow$  Release Agents.

Flame Retardants. The flame resistance of BPA-PC can be increased by incorporating tetrabromobisphenol (see Section 2.2) or by using additives or additive combinations [6]. For example, flame resistance is significantly improved by the addition of small amounts (< 1 wt%) of special salts, such as potassium perfluoro-n-butane-1-sulfonate, sodium 2,4,5-trichloroben-

zenesulfonate, and potassium diphenylsulfone-3-sulfonate [22]–[25]. The tendency to form flaming drips after ignition can be reduced by using branched polycarbonates (see Section 2.2) or by adding small amounts (< 1 wt %) of polytetrafluoroethylene [26].

Light Stabilizers. Ultraviolet light, especially in combination with atmospheric oxygen and moisture, causes decomposition of BPA-PC. Decomposition starts with a photo-Fries rearrangement, which leads to the formation of salicylates, followed by benzophenones [6], [7]. These structures absorb visible light in the shortwavelength region and are thus responsible for the yellowing of polycarbonates. Stabilization against degradation by UV light (i.e., against yellowing) is important for exterior uses and applications and can be achieved by adding small amounts (< 1 wt %) of benzotriazole derivatives [7].

Reinforcement. Glass fibers (< ca. 35 wt%) are generally added to the polycarbonate for reinforcement. They improve rigidity and stiffness, and lower the coefficient of thermal expansion [6], [7], [27].

Miscellaneous Additives. Heat stabilizers (e.g., organic phosphites) can be added to the polycarbonate to prevent thermal oxidation during processing at high temperature [6]. Blowing agents (e.g., 5-phenyltetrazole and phenyldihydroxo-oxadiazonone) can be added during thermoplastic processing into moldings to obtain low-weight foamed structures (→ Foamed Plastics, A11, p. 458) [6]. Transparent or opaque polycarbonates can be obtained in a wide range of colors by using organic dyes and inorganic pigments.

#### 3. Production

#### 3.1. Interfacial Polycondensation

Interfacial polycondensation is currently used for the industrial production of polycarbonates [2], [5], [6]. Bisphenol A is reacted with phosgene at 20-40°C in a two-phase mixture consisting of an aqueous, alkaline phase and an immiscible organic phase. The overall reaction is as follows:

$$\begin{array}{c}
\text{CH}_{3} \\
\text{CH}_{3}
\end{array}$$

$$\begin{array}{c}
\text{CH}_{3} \\
\text{CH}_{3}
\end{array}$$

$$\begin{array}{c}
\text{CI} \\
\text{CH}_{3}
\end{array}$$

The bisphenol A i aqueous phase as sodin phosgene is dissolved i generally consists of cl (e.g., dichloromethane) phase interface to prod which then enter the 20 mol% excess of pl amount of bisphenol A, a small proportion of drolyzed. The hydroly Na<sub>2</sub>CO<sub>3</sub>) enter the aclow pH values (9-11) a genation to minimize r

After the formation a catalyst is added. It (e.g., triethylamine, trillylamine) are preferred at the polycondensation in the polycondensation in the second in the aqueous phase values (9-14).

Monofunctional p phenol or 4-tert-butyly nol A) are added as two-phase mixture belyst, to control the mo pounds then form the polycarbonate bound

Polycarbonate probatchwise in stirred tarcades of stirred tanks which the organic and distributed by shear for polycondensation, the which contains sodiun bonate, is separated for centrifugation. The organic from residual traces of washing with dilute as

The water content [2.76] is also of great importance for the processing of thermoplastic polyesters because water often causes hydrolytic decomposition at high processing temperatures (see p. 241). The equilibrium water content, for a given degree of polymerization  $\bar{P}_n$  must not be exceeded on account of the danger of hydrolytic decomposition. This content can be calculated for high conversions from the approximate formula

$$\bar{P}_{\rm n} = \sqrt{\frac{K}{n_{\rm H_2O}}}$$

 $\bar{P}$  where K is the equilibrium constant and  $n_{\rm H_2O}$  denotes the number of moles of water per mole of monomer. For example, the maximum water content for PETP ( $K \approx 4$ ) with a molecular mass  $M_{\rm p} \approx 10\,000$  ( $\bar{P}_{\rm p} = 100$ ) is 0.01 wt %.

A further criterion for the use of thermoplastic polyesters in the fiber or plastics sector is the intrinsic color. This is usually specified as a blue-yellow value (measured with an electric remission photometer) [2.77].

#### 2.4. Co-Components and Additives [2.78]

Thermoplastic Copolyesters. The dyeability, elasticity, pilling behavior, shrinkage, hydrophilicity, and flame resistance of polyester fibers can be improved by condensation with appropriate comonomers [2.79].

The crystallinity, melting point, glass transition temperature, elasticity, flammability, solubility, and other properties of thermoplastic polyesters used in the plastics sector can be modified by selective co-condensation.

Examples of such copolyesters are glass-clear (amorphous) copolyesters based on 1,4-cyclohexanedimethanol, terephthalic acid, and isophthalic acid (i.e., poly(1,4-cyclohexylenedimethylene terephthalate-co-isophthalate) [26124-27-6] [2.80]); elastic copolyesters based on 1,4-butanediol, poly(tetrahydrofurandiol), and terephthalic acid (i.e., poly(butylene terephthalate-co[multibutylenoxy] terephthalate) [2.53], [2.54]; neopentyl-glycol-containing copolyesters with good solution properties in paint solvents [2.81]; and copolyesters based on 1,4-butanediol, terephthalic acid, and isophthalic acid with relatively low melting points for hotmelt adhesives [2.82]. Thermoplastic copolyesters with elevated glass transition temperatures (and thus improved heat resistance) can be obtained by incorporating heterocyclic diols during condensation [2.83]. For the production of copolyesters, see p. 238.

Additives. Raw polymers are seldom processed as such into semifinished or finished articles. Additives are usually added to the polymers in a process known as compounding or formulation. Compounding processes (e.g., mixing, kneading, extrusion, pelletization) are of great importance because the properties, processing, and use of thermoplastic polymers are substantially determined by the additives (e.g., nucleating agents, fillers, flame retardants, stabilizers, pigments).

Nucleating Agents [2.84], [2.85]. See also → Plastics, Additives, A 20, pp. 500-501. The processibility of PETP in injection molding is mainly determined by its slow crystallization rate and by the associated danger of cold crystallization (tendency to distortion). High molding temperatures (ca. 140°C) and addition of nucleating agents are therefore necessary to accelerate the nucleation rate. Inorganic substances such as talc, magnesium oxide, or clay are added as nucleating agents in concentrations of 0.001-1% with a maximum particle size of 2-3 µm. Organic compounds include salts of aromatic carboxylic acids, fatty acid salts, Montan waxes, and polymers such as polyethylene. The nucleating agents can be added at any stage during PETP production or as a powder to the granulate.

PBT and PBT copolyesters with polytetrahydrofuran generally crystallize so rapidly that nucleation is not necessary.

Glass Fibers [2.86]. See also → Plastics, Additives, A 20, pp. 494-497. The heat resistance, rigidity, and hardness of thermoplastic polyesters can be considerably increased by adding glass fibers or beads. For example, the heat distortion temperature (according to Martens, DIN 53458) of PBT reinforced with glass fiber varies as follows:

Heat distortion temperature, °C 50 75 120 160 190 Glass fiber content, wt % 0 10 20 30 50

The glass reinforcement may be added as beads, ground glass fiber, staple glass fiber, or long glass fiber. Maximum heat resistance, rigidity, and hardness are achieved by adding long glass fibers. These additives are mixed with the thermoplastic polyesters in special extruders in a separate compounding stage; amounts of up to 50% are commonly employed.

Flame Retardants. See also → Flame Retardants, and → Plastics, Additives, A 20, pp. 483-494. Thermoplastic polyesters (PETP and PBT) have a relatively low flammability because they escape the action of the flame due to melting and droplet formation (oxygen index of PBT, 23%; UL 94 rating, HB); see also → Flame Retardants, A 11, p. 127). Fillers and, in particular, glass fiber reinforcement prevent droplet formation, resulting in a sharp increase in flammability (oxygen index of PBT reinforced with 10% glass fiber, 19%). Legislation is increasingly promoting the use of self-extinguishing, nondrip plastics formulations.

Self-extinguishing thermoplastic polyesters are obtained by incorporating ca. 30% of flame retardants, which are usually aromatic halogenated compounds combined

with antimony c [2.88] (see also ples are bromin: [2.90], or ethyle with antimony and antimony c [2.91].

The flame in the production sequent compose

The polybrproducing poly
furans in the e
longer used in C
retardants has g
developments as
such as microe
polyphosphates,
carbonate have
sium compound
be added in sub
fore seriously af

Fully aroma flammability an

Stabilizers.
pp. 461-475. In
polyetheresters:
decomposition [
include stericall;
added to the st
0.5 wt % or are

The antiox nylamine has belate, isophthalat butanediol and i

Pigments | equate heat : carbon black cadmium yellmoplastic pol

Admixture of partially a can be select: other polyme p. 294. PBTs v improved wis are used in c strength can polyethylene tained by ble [2.101].

New alloy maleic anhydromaleic anhydromaleic anhydromaleic application rapplication rapplication

stance) can be obtained by incorcyclic diols during condensation production of copolyesters, see

iw polymers are seldom processed iffinished or finished articles. Adlly added to the polymers in a as compounding or formulation. rocesses (e.g., mixing, kneading, ization) are of great importance perties, processing, and use of olymers are substantially deterditives (e.g., nucleating agents, irdants, stabilizers, pigments).

nts [2.84], [2.85]. See also - Plastics. . 500-501. The processibility of PETP z is mainly determined by its slow crysby the associated danger of cold crysy to distortion). High molding temperaind addition of nucleating agents are to accelerate the nucleation rate. Inorch as tale, magnesium oxide, or clay are agents in concentrations of 0.001-1% varticle size of 2-3 µm. Organic comts of aromatic carboxylic acids, fatty waxes, and polymers such as polyating agents can be added at any stage iction or as a powder to the granulate. copolyesters with polytetrahydrofuran so rapidly that nucleation is not neces-

1.86]. See also → Plastics, Additives, The heat resistance, rigidity, and hard-tic polyesters can be considerably inglass fibers or beads. For example, the perature (according to Martens, DIN orced with glass fiber varies as follows:

perature, °C 50 75 120 160 190 wt% 0 10 20 30 50

forcement may be added as beads, staple glass fiber, or long glass fiber. sistance, rigidity, and hardness are long glass fibers. These additives are moplastic polyesters in special extrud-impounding stage; amounts of up to remployed.

ts. See also → Flame Retardants, and es, A 20, pp. 483-494. Thermoplastic and PBT) have a relatively low se they escape the action of the flame I droplet formation (oxygen index of ating, HB); see also → Flame Retar-Fillers and, in particular, glass fiber ant droplet formation, resulting in a mmability (oxygen index of PBT reinass fiber, 19 %). Legislation is increasuse of self-extinguishing, nondrip plas-

ng thermoplastic polyesters are obing ca. 30% of-flame retardants, which ic halogenated compounds combined with antimony oxide [2.87] or with phosphorus compounds [2.88] (see also  $\rightarrow$  Flame Retardants, A 11, p. 123). Examples are brominated polycarbonates [2.89] and polystyrenes [2.90], or ethylene(tetrabromophthalimide) in combination with antimony oxide. A combination of red phosphorus and antimony oxide is also used, particularly with PETP [2.91].

The flame retardants are not normally added during the production of thermoplastic polyesters, but in a sub-

sequent compounding stage.

The polybrominated diphenyl ethers are suspected of producing polybrominated dibenzodioxins and dibenzofurans in the event of fire [2.92]; they are therefore no longer used in Germany, and interest in halogen-free flame retardants has greatly increased. Up to now, however, only developments and improvements of conventional systems, such as microencapsulated red phosphorus, ammonium polyphosphates, magnesium hydroxide, and magnesium carbonate have been described [2.93], [2.94]. The magnesium compounds have the disadvantage that they have to be added in substantially higher amounts and may therefore seriously affect the polymer properties.

Fully aromatic liquid crystalline polyesters have a low flammability and do not require flame retardants.

Stabilizers. See also → Plastics, Additives, A 20, pp. 461-475. In contrast to PETP and PBT, thermoplastic polyetheresters are extremely sensitive to photooxidative decomposition [2.95] and must be stabilized. Stabilizers include sterically hindered phenols or amines, which are added to the starting substances in an amount of 0.1-0.5 wt % or are incorporated in the polymer melt [2.96].

The antioxidant 4,4'-bis $(\alpha,\alpha'$ -dimethylbenzyl)diphenylamine has been approved by the FDA for use in phthalate, isophthalate, and terephthalate polyesters with 1,4-

butanediol and polytetrahydrofuran.

Pigments [2.97], [2.98]. Pigments with an adequate heat resistance (e.g., titanium dioxide, carbon black, phthalocyanines, quinacridones, cadmium yellow) are suitable for coloring thermoplastic polyesters.

Admixture of Other Polymers. The properties of partially aromatic thermoplastic polyesters can be selectively improved by blending with other polymers. See also, → Polymer Blends, p. 294. PBTs whose impact properties have been improved with polybutadiene graft rubbers are used in car bumper systems [2.99]. Impact strength can also be increased by adding polyethylene [2.100]. Higher flexibility is obtained by blending with polyether elastomers [2.101].

New alloying components such as styrene—maleic anhydride copolymers or acrylonitrile—styrene—acrylate copolymers also expand the application range, particularly of PBT [2.102]. Polymer blends of bisphenol-A-polycarbonate with PBT or PETP have good low-temperature strength and low shrinkage values, they have been commercially successful for several years [2.103].

Blends with polyurethanes and polyamides [2.104] or poly- $\varepsilon$ -caprolactone [2.105] are also described.

#### 2.5. Properties

The properties of thermoplastic polyesters depend primarily on the starting compounds (dicarboxylic acids, diols), their molecular mass, and added fillers. The properties of PETP, PBT, and PDCT as fiber raw materials are described in → Fibers, 4. Synthetic Organic, A 10, pp. 587, 601, 603.

PETP and PBT. The two most important thermoplastic polyesters for the plastics sector, namely PETP and PBT, can be described as partially crystalline polymers. They have a high hardness and rigidity, good creep strength, high dimensional stability, and very good slip and wear behavior [2.106], [2.107]. Whereas PBT occurs almost exclusively in the partially crystalline form, PETP can also be processed into amorphous molded bodies with high transparency; on heating to 70-100°C this transparency is lost due to postcrystallization. Transparency can, however, be retained if the polyester chains are forcibly oriented, for example by biaxial stretching and heat setting (transparent films of PETP,  $\rightarrow$  Films, A11, p. 105).

A special property of PETP is its slow crystallization, which necessitates molding temperatures of ca. 140 °C and the use of a nucleating agent and crystallization accelerator (see p. 240).

PBT and PETP are resistant to water, weak acids and bases, alcohols, ketones, ethers, aliphatic hydrocarbons, and chlorinated aliphatic hydrocarbons at room temperature.

Solvents for PBT and PETP include hexafluoro-2-propanol, hexafluoroacetone, and 2chlorophenol (mixed solvents, see Table 2).

Hydrolysis proceeds rapidly in the melt in the presence of moisture. The dependence of the hydrolysis rate on temperature and moisture content has been investigated [2.108], [2.109].

The most important mechanical, thermal, and electrical properties of PETP and PBT are summarized in Table 3.

Polyetheresters [2.110] – [2.112]. Thermoplastic polyetheresters are block copolymers synthesized from mutually incompatible rigid crys-